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Reg'd PCT 01 APR 2005

REC'D 19 SEP 2003

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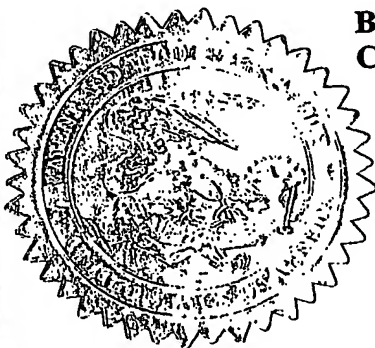
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FILING DATE.

APPLICATION NUMBER: 60/415,636

FILING DATE: October 01, 2002

RELATED PCT APPLICATION NUMBER: PCT/US03/25447

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10/01/02
JC970 U.S. PTO

10-02-02

60415636-1001003
Docket Number 3189R

1011 U.S. PTO
60/415636
10/01/02

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
PROVISIONAL APPLICATION COVER SHEET

Box Provisional Patent Application
Commissioner for Patents
Washington, DC 20231

(A) The attached document is filed as a Provisional Application for patent under 37 CFR 1.53 (c)(1).

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(C) Title: Metal Hydroxide Desiccated Emulsions Used to Prepare Grease

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(E) Docket Number: 3189R

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(G) Fees: Charge the fee for filing of a provisional application, believed to be \$150.00, to Deposit Account No. 12-2275 (The Lubrizol Corporation). Any deficiency or overpayment in fees should be charged or credited to the same account.

(H) 19 Pages of Specification 4 Pages of Claims
2 Sheets of Drawings 1 Pages of Abstract

(I) A duplicate of this Cover Sheet is attached.

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Oct 1, 2002
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I certify that this correspondence is being deposited with the United States Postal Service as Express Mail No. ET019029108US in an envelope addressed to: Box Provisional Application, Commissioner for Patents, Washington, DC 20231, on: October 1, 2002.

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Date: October 1, 2002

3189R

Metal Hydroxide Desiccated Emulsions Used to Prepare Grease

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Field of the Invention

The invention relates to a method of preparing soap thickened lubricating greases using lithium hydroxide in the form of a desiccated lithium dispersion. The use of desiccated metal hydroxide emulsion technology to make the lithium dispersion allows greases to be prepared under milder conditions.

10

Background of the Invention

It is well known that grease manufacturing can be either continuous or non-continuous. Both processes react solid or aqueous lithium hydroxide monohydrate with carboxylic acids in the presence of mineral oil. The reaction of lithium hydroxide monohydrate and the carboxylic acid acts to thicken the mineral oil to produce straight lithium greases. The most commonly used carboxylic acid used in the manufacture of grease is 12-hydroxystearic acid.

Non-continuous and continuous processes to prepare said greases require high temperatures for saponification and high pressure vessels.

20

US patent 2,434,539 relates to a continuous method of preparing an anhydrous grease by initially dehydrating metal hydroxide before addition into a slurry with high molecular weight fatty acid.

US patent 2,444,720 relates to the manufacture of lubricants containing lithium grease by intimately reacting anhydrous lithium hydroxide or lithium hydroxide monohydrate with fatty acids at a temperature in the range 35 to 45 degrees Celsius for sufficient time for 90 weight percent of lithium and fatty acid compounds to form a grease.

25

US patent 2,659,695 relates to the preparation of a grease from an insoluble metal hydroxide and a fatty acid with a water in oil emulsion containing petroleum mahogany sulphonates dissolved in mineral oil.

30

US patent numbers 2,708,659 and 2,868,729 relate to methods of preparing grease by initially dissolving calcium hydroxide in lubricating oil before the addition of the appropriate organic acid. The organic acid used in 2,868,729 is a substituted alkenyl succinic acid, whereas 2,708,659 use acids such as stearic, oleic, tallow etc.

US patent 4,075,234 relates to the use grease manufacture using a concentrated aqueous solution of lithium hydroxide in a liquid reaction mixture comprising an alkyl nitrile.

US patent 4,337,209 relates to a method of preparing soap and greases by reacting an organic carboxylic acid, its esters and mixtures thereof with a concentrated aqueous solution of alkali metal hydroxide in the presence of an inorganic salt, in a liquid reaction medium comprising acetone. The presence of the inorganic salt increases the yield of soap or grease.

US patent 5,948,736 relates to a method of forming a dust free lithium hydroxide monohydrate by coating said hydroxide with 0.1 to 5 weight percent of low melting point or liquid fatty acids or esters. Triglycerides of fatty acids may also be used to coat lithium hydroxide monohydrate. Typically, the liquid fatty acids or esters of the invention have a melting point less than 38 degrees Celsius.

US patent 6,153,563 relates to a method of decreasing environmental hazards associated with lithium hydroxide monohydrate or anhydrous lithium hydroxide in grease manufacture. The technology used is a sealed pouch of a single layer polyolefin film having a thickness of 0.0005 to 0.001 inches capable of melting below 138 degrees Celsius and is soluble in a lubricating oil base. The sealed pouch contains said hydroxide or lithium fatty acid or mixtures thereof for use in preparation of grease.

It would be desirable to have a grease composition and a manufacturing process less environmental hazardous e.g. dust or vapour and produces less foam. Furthermore it would be desirable if the process produced a higher yield using less energy and raw materials.

Brief Description of the Drawings

Figure 1 is a plot temperature programmed thermogravimetric analysis trace for water in oil lithium hydroxide.

Figure 2 is a plot temperature programmed thermogravimetric analysis trace for lithium hydroxide monohydrate.

Summary of the Invention

The present invention provides a grease composition comprising the reaction product of:

- a. a stable dispersion of a metal hydroxide with a number average particle size in the range 20 nanometres to 2 micrometres;
- b. a surfactant with a HLB of less than 10;
- c. a mono or poly- carboxylic acid of 4 to 30 carbon atoms, optionally mono or poly substituted with hydroxyl groups, or alternatively an ester of said carboxylic acid reacted with an alcohol; and
- d. an oil of lubricating viscosity

The invention further provides a manufacturing process for grease with reduced environmental hazards e.g. dust or vapour. The invention further provides a method of preparing grease with an increase yield of viscosity modifying salt per gram of metal and/or carboxylic acid. The invention further provides a metal hydroxide that is substantially anhydrous. The invention further provides a process for grease manufacture resulting in a significant reduction in the amount of foam. The invention further provides a process for producing grease with a significantly shorter reaction time than current processes. The invention further provides a method of preparing grease with reduced environmental hazards, a reduced reaction time, less foam and increased grease yield.

Detailed Description of the Invention

It has been found that a grease composition comprising the reaction product of:

- a. a stable dispersion of a metal hydroxide with a number average particle size in the range 20 nanometres to 2 micrometres;
- b. surfactant with a HLB of less than 10;
- c. a mono or poly- carboxylic acid of 4 to 30 carbon atoms, optionally
5 mono or poly substituted with hydroxyl groups, or alternatively an ester of said carboxylic acid reacted with an alcohol; and
- d. an oil of lubricating viscosity

Metal Hydroxide

10 Stable dispersions of metal hydroxides herein is meant to encompass finely dispersed metal hydroxide particles which remain substantially in suspension (e.g. colloidally stable) for at least one day, preferably one week, more preferably at least two months, even more preferably at least six months and most preferably one year or more.

15 Stable dispersions of metal hydroxides of the invention have a number average particle size in the range 20 nanometres to 2 micrometres, preferably 40 nanometres to 1.5 micrometres, more preferably 75 nanometres to 1 micrometres, even more preferably 100 to 600 nanometres and most preferably 200 to 500 nanometres.

20 The metal hydroxide is a mono- or di- or tri- valent metal or a mixture thereof. Preferably the metal hydroxide is an alkali metal, an alkaline earth metal, aluminium or a mixture thereof. More preferably the alkali metal hydroxide is lithium, sodium, potassium, the alkaline earth metal is calcium, magnesium or barium. Most preferably, the metal hydroxide is lithium hydroxide.

25 The metal hydroxide of the invention is in the form of $M(OH)_{1-3} \cdot xH_2O$, wherein M is a mono- or di- or tri- valent metal ion; "1-3" means 1, 2, or 3 hydroxyl groups, and x can be a fraction in the range 0 to 1. When $x=1$ the metal hydroxide is in the form of the monohydrate. When x is greater than zero and less than 1, the lithium hydroxide is partially, substantially or wholly
30 anhydrous. Partially anhydrous lithium hydroxide is when x is in the range 0.9 to 0.5, preferably 0.85 to 0.55, most preferably 0.6 to 0.7. Substantially anhydrous metal hydroxide has x less than 0.5, preferably less than 0.3, even

more preferably less than 0.1 but greater than 0.02. Wholly anhydrous metal hydroxide has x in the range 0.02 to 0, preferably x is in the range 0.01 to 0, even more preferably x is 0. Most preferably the metal hydroxide is substantially or wholly anhydrous.

5 The amount of the dispersion of metal hydroxide in oil present in the invention is generally in the range 0.5 to 20, preferably 1 to 15, more preferably 3 to 12, and most preferably 4 to 10 weight percent based on the weight of the grease if fairly concentrated metal hydroxide dispersions are used to make the grease. The metal hydroxide can be from about 1 or 5 wt.% to about 60 wt.%
10 of the dispersion depending on a variety of conditions that affect the amount of dispersed phase. Multiple emulsifications of a metal hydroxide solution into the oil, followed by desiccation can increase the metal hydroxide concentration. Also the dispersion can be diluted with oil. All components of the grease listed hereafter will be based on the weight of the grease unless specified otherwise.

15 The lithium hydroxide used in the prior art is usually commercially available solid monohydrates. This solid produces a dust when handled which causes choking and is extremely irritating, even in trace amounts. Large amounts of lithium hydroxide monohydrate are used in the continuous or non-continuous manufacture of lithium grease and the irritating dust is an
20 environmental hazard during handling and mixing operations. Furthermore, bulk powders of lithium hydroxide monohydrate can easily be spilled by the user, causing waste, as well as possible respiratory irritation. Also, waste can occur while loading the reactor through spillage, resulting in an insufficient charge, yielding a grease composition below the desired specifications.

25 The granules or powders of lithium hydroxide monohydrate of the prior art with number average particle size above above 2 or 5 microns have a tendency to agglomerate and cake after contact with water or when stored in areas of high humidity. This caking diminishes the amount of exposed surface area that can be initially contacted by the lubricating oil base stock during the
30 saponification reaction; thereby slowing the reaction. The caking of the lithium hydroxide and the severe reaction conditions result in a low production capacity and the use of excessive amounts of energy and extended reaction times.

Current continuous or non-continuous processes also tend to produce excessive amounts of foam.

Surfactants

The surfactants of the desiccated emulsion or dispersion have emulsifier and/or dispersant properties and comprise ionic or non-ionic compounds, having a hydrophilic lipophilic balance (HLB) in the range less than 10, desirably 1 to 8, and most preferably 2.5 to 6. Those skilled in the art will appreciate that combinations of surfactants may be used with individual HLB values outside of the ranges 1 to 8 or 2.5 to 6, provided that the composition of the final surfactant blend is within these ranges. The amount of the surfactant to form the metal hydroxide dispersion in oil in the final grease can be a 1 or 2 wt.% based on the weight of the metal hydroxide to 100 or 200 wt.% based on the metal hydroxide component in the grease.

Examples of these surfactants suitable for the invention are disclosed in McCutcheon's Emulsifiers and Detergents, 1993, North American & International Edition. Generic examples include alkanolamides, alkylarylsulphonates, amine oxides, poly(oxyalkylene) compounds, including block copolymers comprising alkylene oxide repeat units (e.g., Pluronic™), carboxylated alcohol ethoxylates, ethoxylated alcohols, ethoxylated alkyl phenols, ethoxylated amines and amides, ethoxylated fatty acids, ethoxylated fatty esters and oils, fatty esters, glycerol esters, glycol esters, imidazoline derivatives, lecithin and derivatives, lignin and derivatives, monoglycerides and derivatives, olefin sulphonates, phosphate esters and derivatives, propoxylated and ethoxylated fatty acids or alcohols or alkyl phenols, sorbitan derivatives, sucrose esters and derivatives, sulphates or alcohols or ethoxylated alcohols or fatty esters, polyisobutylene succinimide and derivatives, sulphonates of dodecyl and tridecyl benzenes or condensed naphthalenes or petroleum, sulphosuccinates and derivatives, and tridecyl and dodecyl benzene sulphonic acids.

In one embodiment the surfactant of the invention is a polyisobutylene succan derivative such as a polyisobutylene succinimide or derivatives. Typical derivatives of polyisobutylene succans include hydrolyzed, esters or diacids. Polyisobutylene succan derivatives are preferred to make the metal hydroxide

dispersions. A large group of polyisobutylene succan derivatives are taught in US 4,708,753, herein incorporated by reference.

In one embodiment the surfactant of the invention is an alkylated benzene sulphonate of an alkali metal or alkaline earth metal. The alkyl group contains 8 to 20 and most preferably 10 to 15 carbon atoms. Most preferably the alkyl group is dodecyl. The alkali metal is lithium, potassium or sodium; whereas the alkaline earth metal is calcium or magnesium. Most preferably the metal is calcium.

Mono or Poly-carboxylic Acid(s)

The carboxylic acid may be any combination of a mono or polycarboxylic; branched alicyclic, or linear, saturated or unsaturated, mono or poly-hydroxy substituted or unsubstituted carboxylic acid, acid chloride or the ester of said carboxylic acid with an alcohol such as an alcohol of 1 to 5 carbon atoms. The carboxylic acid has 4 to 30, preferably 8 to 27, more preferably 12 to 24 and most preferably 16 to 20 carbon atoms. The carboxylic acids having this number of carbon atoms are generally associated with an HLB (hydrophile to lipophile balance) of 10 or more, preferably 12 or more and more preferably 15 or more when converted to their salt form. Generally an HLB of 10 or more is associated with significant attraction to the water phase (hydrophilic) relative to the attraction for the lipophilic phase (oil phase).

In one preferred embodiment the carboxylic acids are hydroxy substituted or unsubstituted alkanolic acids. Typically, the carboxylic acids will have 4 to 30 carbon atoms, more preferably 12 to 24 and most preferably 16 to 20. Preferably the carboxylic acid is a hydroxystearic acid or esters of these acids such as 9-hydroxy, 10-hydroxy or 12-hydroxy, stearic acid, and most preferably 12-hydroxy stearic acid.

Other saturated carboxylic acids suitable for the invention include capric acid, lauric acid, myristic acid, palmitic acid, arachidic acid, behenic acid and lignoceric acid.

Unsaturated carboxylic acids suitable for the invention include undecylenic acid, myristoleic acid, palmitoleic acid, oleic acid, gadoleic acid, elaidic acid, cis-eicosenoic acid, erucic acid, nervonic acid, 2,4-hexadienoic

acid, linoleic acid, 12-hydroxy tetradecanoic acid, 10-hydroxy tetradecanoic acid, 12-hydroxy hexadecanoic acid, 8-hydroxy hexadecanoic acid, 12-hydroxy icosanic acid, 16-hydroxy icosanic acid 11,14-eicosadienoic acid, linolenic acid, cis-8,11,14-eicosatrienoic acid, arachidonic acid, cis-5,8,11,14,17-eicosapentenoic acid, cis-4,7,10,13,16,19-docosahexenoic acid, all-trans-retinoic acid, ricinoleic acid lauroleic acid, eleostearic acid, licanic acid, citronelic acid, nervonic acid, abietic acid, and abscisic acid. Most preferred acids are palmitoleic acid, oleic acid, linoleic acid, linolenic acid, licanic acid and eleostearic acid.

The amount of carboxylic acid present in the invention is in the range 3 to 30, preferably 3 to 25, more preferably 4 to 20, and most preferably 5 to 18 weight percent.

Oil of Lubricating Viscosity

The lubricating compositions and functional fluids of the present invention are based on diverse oils of lubricating viscosity, including natural and synthetic lubricating oils and mixtures thereof. Synthetic oils may be produced by Fischer-Tropsch reactions including oils formed from gas to liquid reactions.

Natural oils useful in making the inventive lubricants and functional fluids include animal oils and vegetable oils (e.g., castor oil, lard oil) as well as mineral lubricating oils such as liquid petroleum oils and solvent-treated or acid-treated mineral lubricating oils of the paraffinic, naphthenic or mixed paraffinic-naphthenic types. Oils of lubricating viscosity derived from coal or shale are also useful. Synthetic lubricating oils are useful and include hydrocarbon oils such as polymerised and interpolymersised olefins (e.g., polybutylenes, polypropylenes, propyleneisobutylene copolymers,); poly(1-hexenes), poly(1-octenes), poly(1-decenes), and mixtures thereof; alkylbenzenes (e.g., dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di-(2-ethylhexyl)-benzenes,); polyphenyls (e.g., biphenyls, terphenyls, alkylated polyphenyls,); alkylated diphenyl ethers and alkylated diphenyl sulfides and the derivatives, analogs and homologs thereof.

Alkylene oxide polymers and interpolymers and derivatives thereof where the terminal hydroxyl groups have been modified by esterification, and etherification, constitute another class of known synthetic lubricating oils that can be used. These are exemplified by the oils prepared through
 5 polymerisation of ethylene oxide or propylene oxide, the alkyl and aryl ethers of these polyoxyalkylene polymers (e.g., methyl-polyisopropylene glycol ether having a number average molecular weight of 1000, diphenyl ether of polyethylene glycol having a molecular weight of 500-1000, diethyl ether of polypropylene glycol having a molecular weight of 1000-1500) or mono- and
 10 polycarboxylic esters thereof, for example, the acetic acid esters, mixed C_{3-8} fatty acid esters, or the C_{13} Oxo acid diester of tetraethylene glycol.

Another suitable class of synthetic lubricating oils that can be used comprises the esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, alkyl succinic acids, alkenyl succinic acids, maleic acid, azelaic acid, suberic
 15 acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkyl malonic acids, and alkenyl malonic acids) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoether, and propylene glycol) Specific examples of these esters include dibutyl adipate, di-(2-ethylhexyl) sebacate, di-n-hexyl
 20 fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, dieicosyl sebacate, the 2-ethylhexyl diester of linoleic acid dimer, and the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid.

25 Esters useful as synthetic oils also include those made from C_5 to C_{12} monocarboxylic acids and polyols such as neopentyl glycol, trimethylol propane, and pentaerythritol, or polyol ethers such as dipentaerythritol, and tripentaerythritol.

30 Silicon-based oils such as the polyalkyl-, polyaryl-, polyalkoxy-, or polyaryloxy-siloxane oils and silicate oils comprise another useful class of synthetic lubricants (e.g., tetraethyl silicate, tetraisopropyl silicate, tetra-(2-ethylhexyl)silicate, tetra-(4-methylhexyl)silicate, tetra-(p-tert-butylphenyl)

silicate, hexyl-(4-methyl-2-pentoxo)disiloxane, poly(methyl) siloxanes, and poly-(methylphenyl)siloxanes). Other synthetic lubricating oils include liquid esters of phosphorus-containing acids (e.g., tricresyl phosphate, trioctyl phosphate, and the diethyl ester of decane phosphonic acid), and polymeric tetrahydrofurans.

Unrefined, refined and re-refined oils, either natural or synthetic (as well as mixtures of two or more of any of these) of the type disclosed hereinabove can be used in the lubricants of the present invention. Unrefined oils are those obtained directly from a natural or synthetic source without further purification treatment. For example, a shale oil obtained directly from retorting operations, a petroleum oil obtained directly from primary distillation or ester oil obtained directly from an esterification process and used without further treatment would be an unrefined oil. Refined oils are similar to the unrefined oils except they have been further treated in one or more purification steps to improve one or more properties. Many such purification techniques are known to those skilled in the art such as solvent extraction, secondary distillation, acid or base extraction, filtration, percolation, re-refined oils are obtained by processes similar to those used to obtain refined oils applied to refined oils which have been already used in service. Such re-refined oils are also known as reclaimed or reprocessed oils and often are additionally processed by techniques directed to removal of spent additives and oil breakdown products.

Oils of lubricating viscosity can also be defined as specified in the American Petroleum Institute (API) Base Oil Interchangeability Guidelines. The five base oil groups are as follows:

Base Oil Category	Sulphur (%)		Saturates (%)	Viscosity Index
Group I	>0.03	and/or	<90	80-120
Group II	≤0.03	and	≥90	80-120
Group III	≤0.03	and	≥90	≥120
Group IV	All polyalphaolefins (PAOs)			
Group V	All others not included in Groups I, II, III, or IV			

Groups I, II, and III are mineral oil base stocks. Preferably the oil of lubricating viscosity is a Group I, II, III, IV, or V oil or mixtures thereof. More preferably, the oil of lubricating viscosity is a Group I, II or III oil or mixtures thereof.

The amount of oil of lubricating viscosity is present in the range 50 to 96.5, preferably 60 to 94, more preferably 68 to 90 and most preferably 72 to 86 weight percent.

Optional Grease Additives

Metal Deactivators

Metal deactivators useful in lubricating oil compositions are known in the art and include derivatives of benzotriazoles, benzimidazole, 2-alkyldithiobenzimidazoles, 2-alkyldithiobenzothiazoles, 2-(N,N-dialkyldithiocarbamoyl)-benzothiazoles, 2,5-bis(alkyl-dithio)-1,3,4-thiadiazoles, 2,5-bis(N,N-dialkyldithiocarbamoyl)-1,3,4-thiadiazoles, 2-alkyldithio-5-mercapto thiadiazoles or mixtures thereof.

A particularly preferred class of metal deactivators are benzotriazoles. The benzotriazole compounds include hydrocarbyl substitutions at one or more of the following ring positions 1- or 2- or 4- or 5- or 6- or 7- benzotriazoles. The hydrocarbyl groups contain 1 to 30 carbons, more preferably 1-15 carbons; even more preferably 1-7 carbons and, most preferably the metal deactivator is 5-methylbenzotriazole.

The metal deactivators are present in the range of 0 to 5 weight percent. More preferably metal deactivators are present in the range 0.0002 to 2 weight percent. Most preferably metal deactivators are present in the range 0.001 to 1 weight percent.

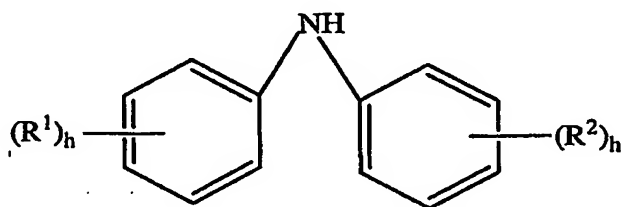
The Antioxidant

Antioxidants suitable for the invention include a variety of chemical types including phenate sulfides, phosphosulfurised terpenes, sulfurised esters, aromatic amines, and hindered phenols.

A particularly preferred antioxidant is alkylated sterically hindered phenols. Typically the alkylated groups are independently branched or linear alkyl groups containing 1 up to 24 carbon atoms, preferably 4 to 18 carbon atoms

and most preferably from 4 to 12 carbon atoms. Alkylated groups may be either straight chained or branched chained; branched chained is generally preferred. Preferably the phenol is a butyl substituted phenol containing 2 t-butyl groups. When the t-butyl groups occupy the 2,6-position, that is, the phenol is sterically hindered. Additionally the phenols may have additional substitution in the form of a hydrocarbyl, or a bridging group between two such aromatic groups. Bridging groups in the para position include $-\text{CH}_2-$ (methylene bridge) and $-\text{CH}_2\text{OCH}_2-$ (ether bridge).

Another class of preferred antioxidants is diphenylamines. These compounds can be represented by the formula:



wherein R^1 and R^2 are independently a hydrogen or an arylalkyl group or a linear or branched alkyl group containing 1 to 24 carbon atoms and h is independently 0, 1, 2, or 3, provided that at least one aromatic ring contains an arylalkyl group or a linear or branched alkyl group. Preferably R^1 and R^2 are alkyl groups containing from 4 to 20 carbon atoms. A preferred embodiment is an alkylated diphenylamine such as mono- or di-nonylated diphenylamine.

Antioxidants are present in the range of 0 to 12 weight percent. More preferably antioxidants are present in the range of 0.1 to 6 weight percent. Most preferably antioxidants are present in the range of 0.25 to 3 weight percent.

Antiwear Agents

The lubricant may additionally contain an antiwear agent. Useful antiwear agents include but are not limited to a metal thiophosphate, especially a zinc dialkyldithiophosphate; a phosphoric acid ester or salt thereof; a phosphite; and a phosphorus-containing carboxylic ester, ether, or amide. A more detailed discussion and examples of phosphorus containing compounds suitable as antiwear agents is discussed in European patent 612 839.

Rust Inhibitors

Rust inhibitors are known in the art and include amine salts of carboxylic acids such as octylamine octanoate, condensation products of dodecenyl succinic acid or anhydride and a fatty acid such as oleic acid with a polyamine, e.g. a polyalkylene polyamine such as triethylenetetramine, and half esters of alkenyl succinic acids in which the alkenyl radical contains 8 to 24 carbon atoms with alcohols such as polyglycols.

The rust inhibitors are present in the range of 0 to 4 weight percent. More preferably the rust inhibitors are present in the range of 0.02 to 2 weight percent. Most preferably the rust inhibitors are present in the range of 0.05 to 1 weight percent.

Extreme Pressure Agents

Extreme pressure (EP) agents that are soluble in the oil include a sulphur or chlorosulphur EP agent, a chlorinated hydrocarbon EP agent, or a phosphorus EP agent, or mixtures thereof. Examples of such EP agents are chlorinated wax, organic sulphides and polysulphides, such as benzyldisulphide, bis-(chlorobenzyl) disulphide, dibutyl tetrasulphide, sulphurised sperm oil, sulphurised methyl ester of oleic acid, sulphurised alkylphenol, sulphurised dipentene, sulphurised terpene, and sulphurised Diels-Alder adducts; phosphosulphurised hydrocarbons, such as the reaction product of phosphorus sulphide with turpentine or methyl oleate, phosphorus esters such as the dihydrocarbon and trihydrocarbon phosphites, *i.e.*, dibutyl phosphite, diheptyl phosphite, dicyclohexyl phosphite, pentylphenyl phosphite; dipentylphenyl phosphite, tridecyl phosphite, distearyl phosphite and polypropylene substituted phenol phosphite, metal thiocarbamates, such as zinc dioctyldithiocarbamate and barium heptylphenol diacid, such as zinc dicyclohexyl phosphorodithioate and the zinc salts of a phosphorodithioic acid combination may be used.

The oil soluble extreme pressure agents are present in the range of 0 to 10 weight percent. More preferably the extreme pressure agents are present in the range 0.25 to 5 weight percent. Most preferably extreme pressure agents are present in the range 0.5 to 2.5 weight percent.

A method of producing a grease composition comprising: a stable dispersion of metal hydroxide present in the range 0.5 to 20 weight percent prepared by removing the solvent from an emulsion of metal hydroxide and solvent in oil, the amount of alkanoic acid present in the range 3 to 30 weight percent and the amount of oil of lubricating viscosity present in the range 50 to 96.5 weight percent to obtain a mixture, said mixture is further treated with a saponification stage and a finishing amount of oil of lubricating viscosity to impart the desired viscosity.

Solvents suitable for forming the metal hydroxide desiccated dispersion of the invention include ionised or deionised water, acetone, and lower alcohols. Typically lower alcohols have 1 to 5 carbon atoms, preferably 1 to 3 carbon atoms. The Exemplary examples include methanol, ethanol, propan-1-ol, propan-2-ol and prop-1-enol. In some instances the carbon chains can have additional substitutions such as halogens or additional hydroxy functionality.

The solvent content of said desiccated dispersion of metal hydroxide is 0.1 to 20, preferably 0.2 to 10, most preferably 0.3 to 5 weight percent based on the weight of metal hydroxide.

Said method of producing a grease composition allows for less severe reaction conditions compared to known method. As a consequence the reaction temperature to form the metal salt of the carboxylic acid grease thickener may be reduced to a temperature in the range of 80 to 215, preferably 90 to 190, more preferably 110 to 180 and most preferably 120 to 170 degrees Celsius.

Said method of producing a grease composition or the metal salt component thereof wherein the reaction time is reduced by 20 to 90, preferably 30 to 80, more preferably 35 to 70, even more preferably 40 to 60 and most preferably 45 to 55 percent as compared to a control using a powdered form of said metal hydroxide. Those skilled in the art will appreciate that the reduction in reaction time is related to the degree of hydration of the metal hydroxide. Higher degrees of hydration will slow the rate of reaction. Thus, the presence of excessively hydrated metal hydroxide is preferably avoided herein to ensure the reduction in reaction time.

Said method of producing a grease composition wherein the amount of foam produced is reduced by 2 to 100, preferably 20 to 95, more preferably 30

Example 1 – Preparation of Water in Oil/ Desiccated Lithium Hydroxide

A 6.6 weight percent lithium hydroxide solution is prepared in deionised water. The solution is placed into a Waring blender with 9 weight percent of polyisobutylene succinimide (an approximately 1550 molecular weight polyisobutylene succan reacted with triethyltetraamine) solubilised in 100N API Group 2 base oil, $4.05 \text{ mm}^2\text{s}^{-1}$ (cSt) at 100°C . The overall mixture contains 6.6 weight percent lithium hydroxide, 53.41 weight percent deionised water, 9 weight percent of polyisobutylene succinimide and 31 weight percent of base oil. The water to oil phase ratio is 60:40. The Waring blender is used to blend the starting material using high shear for 10 minutes. The sample is cooled for 10 minutes. The shearing process is repeated twice more until water in oil emulsion is prepared.

The water in oil emulsion is slowly added into a vacuumed environment at 110 degrees Celsius over a period of time to reduce water content to less than 1 weight percent. The final product has a TBN of 203, 2.4 weight percent lithium corresponding to 8.2 weight percent of anhydrous lithium hydroxide.

Test 1 Temperature Programmed Thermal Analysis

A 20.78 milligram sample of desiccated LiOH dispersion is placed in a sample holder and inserted into a 2950 TGA produced by TA Instruments. The sample is stored under nitrogen at 30 degrees Celsius until constant weight. The sample is then heated at 5 degrees Celsius per minute up to 750 degrees Celsius and constant mass in nitrogen.

Comparative Example 1 of 19.96 milligrams of lithium hydroxide monohydrate is treated as described above.

The thermal analysis traces for Example 1 and Comparative Example 1 are shown in Figures 1 and 2 respectively. Comparative Example 1 loses 39.5 weight percent at approximately 126 degrees Celsius and this equates to the removal of water of crystallisation. Example 1 does not lose water of crystallisation indicating the sample is substantially or wholly anhydrous.

Example 2 - Preparation of Grease Using Desiccated Lithium Hydroxide Dispersion

46.17 grams of water in oil lithium hydroxide, 44.17 grams of 12-hydroxystearic acid and 213.82 grams of 100N API Group 3 base oil, 13 mm²s⁻¹ (cSt) at 100°C are placed in a 1 kilogram round bottomed glass reaction flask, fitted with a steel stirrer, nitrogen inlet, Dean and Stark attachment with a water cooled glass condenser fitted, and a temperature probe connected to an electronic temperature control device. The contents of the flask are stirred at 500rpm at 80 degrees Celsius. Upon soap formation stirrer speed is increased to 1000rpm and the temperature is increased to 215 degrees Celsius at a rate of 5 degrees Celsius per minute. The temperature is kept constant at 215 degrees Celsius for 15 minutes. Soap form base oil is added over a period of 10 minutes.

The temperature is decreased to 188 degrees Celsius where the reaction mixture becomes immobile due to soap formation. The temperature is decreased to 150 degrees Celsius where the finish oil is added over a period of 10 minutes. The reaction is then allowed to cool to 80 degrees Celsius.

The reaction described above produces a NLGI number 3 grease with a reaction time of 105 minutes, minimal foaming during formation, lower than expected soap content of 8.3 percent, WP₆₀ = 235mm⁻¹ and a Dropping Point of 200 degrees Celsius. The Dropping Point method is described in ASTM D2265.

Comparative Example 2 - Grease Produced by Conventional Lithium Hydroxide

9.72 grams of lithium hydroxide monohydrate, 66.20 grams of 12-hydroxystearic acid and 341.00 grams of 100N API Group 3 base oil, 13 mm²s⁻¹ (cSt) at 100°C are placed in a 1 kilogram round bottomed glass reaction flask fitted with a steel stirrer, nitrogen inlet, Dean and Stark attachment with a water cooled glass condenser fitted, and a temperature probe connected to an electronic temperature control device. The contents of the flask are stirred at 750rpm at 80 degrees Celsius. Upon soap formation stirrer speed is increased to 900rpm and the temperature is increased to 105 degrees Celsius where high degree of foaming. The temperature is raised to 115 degrees Celsius at a rate of

1 degree Celsius per minute. The temperature is increased to 205 degrees Celsius at a rate of 2 degree Celsius per minute and held for 30 minutes. The temperature is increased to 215 degrees Celsius and soap form base oil is added over a period of 10 minutes.

5 The temperature is decreased to 188 degrees Celsius where the reaction mixture becomes immobile due to soap formation. The temperature is decreased to 150 degrees Celsius where the finish oil is added over a period of 10 minutes. The reaction is then allowed to cool to 80 degrees Celsius.

10 The reaction described above produces a NLGI number 3 grease with a reaction time of 185 minutes, high degree of foaming during formation, soap content of 9 percent, $WP_{60} = 209\text{mm}^{-1}$ and a Dropping Point of 200 degrees Celsius. The Dropping Point method is described in ASTM D2265.

15 While the invention has been explained in relation to its preferred embodiments, it is to be understood that various modifications thereof will become apparent to those skilled in the art upon reading the specification. Therefore, it is to be understood that the invention disclosed herein is intended to cover such modifications as fall within the scope of the appended claims.

20 Each of the documents referred to above is incorporated herein by reference. Except in the Examples, or where otherwise explicitly indicated, all numerical quantities in this description specifying amounts of materials, reaction conditions, molecular weights, number of carbon atoms, are to be understood as modified by the word "about." Unless otherwise indicated, each chemical or composition referred to herein should be interpreted as being a commercial grade material which may contain the isomers, by-products, 25 derivatives, and other such materials which are normally understood to be present in the commercial grade. However, the amount of each chemical component is presented exclusive of any solvent or diluent oil, which may be customarily present in the commercial material, unless otherwise indicated. It is to be understood that the upper and lower amount, range, and ratio limits set 30 forth herein may be independently combined. Similarly, the ranges and amounts for each element of the invention can be used together with ranges or amounts for any of the other elements. As used herein, the expression

"consisting essentially of" permits the inclusion of substances that do not materially affect the basic and novel characteristics of the composition under consideration.

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Claims

What is claimed is:

- 5 1. A grease composition comprising the reaction product of:
 - a.a stable dispersion of a metal hydroxide with a number average particle size in the range 20 nanometres to 2 micrometres;
 - b. a surfactant with a HLB of less than 10;
 - 10 c.a mono or poly- carboxylic acid of 4 to 30 carbon atoms, optionally mono or poly substituted with hydroxyl groups, or alternatively an ester of said carboxylic acid reacted with an alcohol; and
 - d. an oil of lubricating viscosity
- 15 2. The composition of claim 1, wherein the amount of a stable dispersion of metal hydroxide is present in the range 0.5 to 20 weight percent, the amount of carboxylic acid is present in the range 3 to 30 weight percent and the amount of oil of lubricating viscosity is present in the range 50 to 96.5 weight percent.
- 20 3. The composition of claim 2, wherein the metal of the metal hydroxide is present in the range 2 to 16 weight percent.
4. The composition of claim 1, wherein the metal hydroxide is substantially anhydrous.
- 25 5. The composition of claim 1, wherein the metal of the metal hydroxide is a monovalent metal, a divalent metal, a trivalent metal or a mixture thereof.
6. The metal hydroxide of claim 3, wherein the metal of the metal hydroxide is an alkali metal, an alkaline earth metal, aluminium or a mixture thereof.
- 30

7. The composition of claim 1, wherein the carboxylic acid is selected from the group consisting of a branched or linear carboxylic acid with 4-30 carbons, an ester of a branched or linear carboxylic acid with 4-30 carbons reacted with an alcohol of 1-5 carbon atoms or mixtures thereof.

5

8. The carboxylic acid of claim 7, wherein the carboxylic acid is selected from the group consisting of a substituted or unsubstituted stearic acid.

9. The grease composition of claim 1 further comprising: at least one
10 compound selected from the group consisting of an antiwear agent, an antioxidant, a metal deactivator, a rust inhibitor and an extreme pressure additive.

10. A method of producing a grease composition comprising: a stable
15 dispersion of metal hydroxide present in the range 0.5 to 20 weight percent prepared by removing the solvent from an emulsion of metal hydroxide and solvent in oil, the amount of mono or poly-carboxylic acid present in the range 3 to 30 weight percent and the amount of oil of lubricating viscosity present in the range 50 to 96.5 weight percent to obtain a mixture, said mixture is further
20 treated with a saponification stage and a finishing amount of oil of lubricating viscosity to impart the desired viscosity.

11. The process of claim 10, wherein the solvent content of said dispersion of metal hydroxide is 0.1 to 20 weight percent based on the weight of metal
25 hydroxide.

12. The process of claim 10, wherein the reaction time is reduced by 20 to 90 percent as compared to a control using a powdered form of said metal hydroxide.

30 13. The process of claim 10, wherein the reaction temperature is in the range of 80 to 215 degrees Celsius.

14. The process of claim 10, wherein the amount of foam produced is reduced by 2 to 100 percent as compared to a control using a powdered form of said metal hydroxide.
- 5 15. The process of claim 10, wherein the grease composition is prepared by a non-batch process.
16. The process of claim 10, wherein the grease yield is increased per gram of metal hydroxide and gram of alkanolic acid as determined by any NLGI grades
10 1-6 achieved with at least 8 percent by weight less of said metal hydroxide and at least 8 percent by weight less carboxylic acid as compared to a control of the same grade prepared from the same chemical using a powdered form of said metal hydroxide.
- 15 17. A process to prepare a solid grease thickener comprising the reaction product of:
 - a) a stable dispersion of a metal hydroxide with a number average particle size in the range 20 nanometres to 2 micrometres;
 - b) a surfactant with a HLB of less than 10;
 - 20 c) a mono or poly-carboxylic acid of 4 to 30 carbon atoms, optionally mono or poly hydroxy substituted or its ester reaction product with an alcohol; and
 - d) a suitable solvent
 - e) and optionally, a complexing acid such as adipic acid or azelaic acid
 - 25 f) and following formation of the solid thickener the solvent is removed by evaporation, filtration.
18. A lubricating grease made wherein the product of claim 17 is dispersed in a lubricating fluid.
- 30 19. A process to form a lubricating grease comprising the reaction product of:

- a) a stable dispersion of a metal hydroxide with a number average particle size in the range 20 nanometres to 2 micrometres;
 - b) a surfactant with a HLB of less than 10;
 - c) a mono or poly-carboxylic acid of 4 to 30 carbon atoms, optionally
5 mono or poly hydroxy substituted or its ester formed by reaction with an alcohol; and
 - d) a suitable solvent, and
 - e) optionally, a complexing acid such as adipic acid or azeleic acid
- and following formation of the solid thickener the solvent is exchanged with a
10 lubricating fluid.

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Abstract

5 The invention provides a grease composition comprising a stable
dispersion of a metal hydroxide with a number average particle size in the
range 20 nanometres to 2 micrometres, a surfactant with a HLB of less than 10,
a mono or poly-carboxylic acid, and an oil of lubricating viscosity. The method
of preparing a grease composition is also disclosed with benefits including a
reduction in reaction time, amount of foam produced and environmental
10 hazards.

**Figure 1: Temperature Programmed TGA for Water in Oil Emulsion
of Lithium Hydroxide**

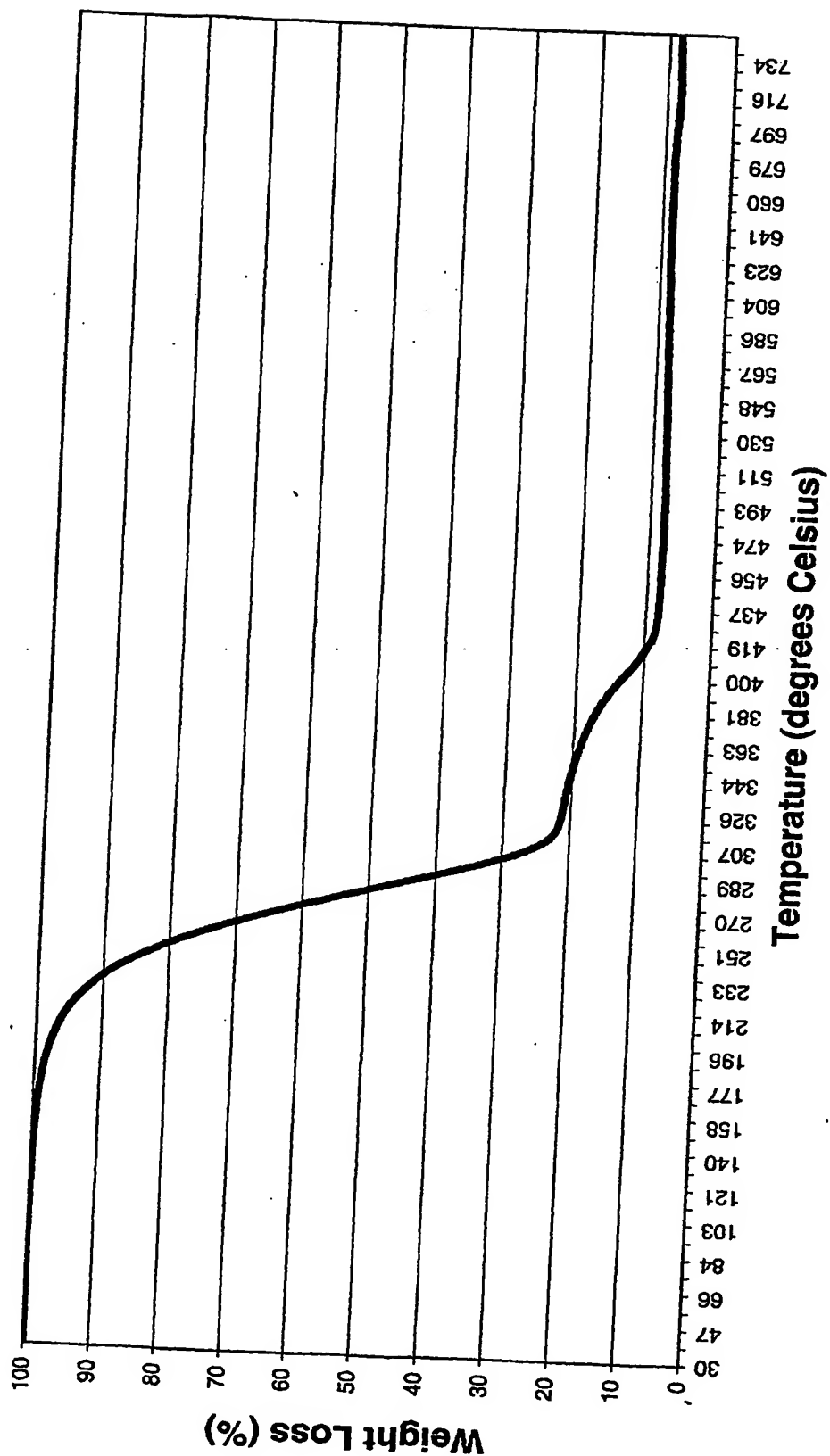
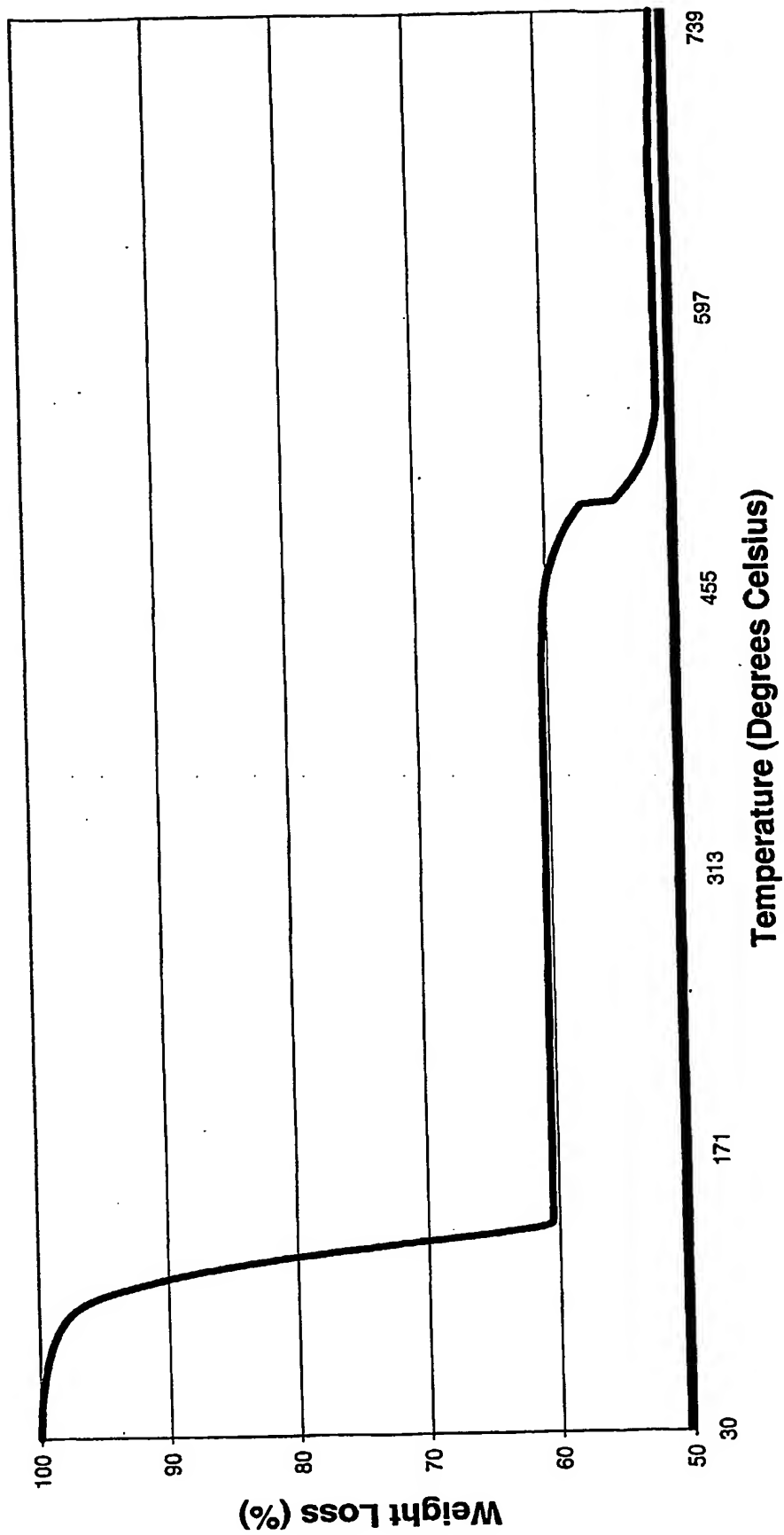


Figure 2: Temperature Programmed TGA for Lithium Hydroxide Monohydrate



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